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(54) Method of treating synthetic
resin shaped articles

(57) A method for the improvement of the antistatic performance of a synthetic resin shaped article comprises two steps, the first of which is the formation of a cross-linked layer at the surface of the shaped article, and the second of which is the exposure of the thus-cross-linked surface to low temperature plasma produced in an atmosphere containing a gaseous silicon-containing compound which may be a silane compound or a low molecular weight vaporisable siloxane compound, to form a plasma-polymerised surface film of the silicon compound on the cross-linked layer.

SPECIFICATION

Synthetic resin shaped articles

- 5 The present invention relates to a method for the improvement of the antistatic performance of a shaped article of a synthetic resin or, more particularly, to a method for improving the antistatic performance, i.e. decreasing the surface resistivity and accumulation of static electricity, on the surface of a shaped article of a synthetic resin by means of low temperature plasma treatment. 5
- Shaped articles of various kinds of synthetic resins are widely used in a variety of fields not only as a general-purpose product but also for several specific applications, because they are 10 manufactured usually with high productivity and outstandingly low costs in addition to their excellent properties such as electric insulation. This desirable property of high electric insulation or, in particular, high surface resistivity, of synthetic resin shaped articles, however, causes several difficult problems due to the accumulation of static electricity on the surface, accompanied by the relatively small dielectric loss thereof. For example, the surface of synthetic resin 15 shaped articles rapidly loses its appearance by the deposition of dusts and dirt thereon. Human bodies coming into contact with an electrostatically-charged surface of such a shaped article can receive electric shocks, and spark discharges between charged surfaces sometimes cause serious problems of disturbance, i.e. noise generation, in electronic circuits. 15
- 20 Therefore, it is very important to develop a convenient and efficient method for the improvement of the antistatic performance of, or for the decrease of the accumulation of static electricity on, the surface of a synthetic resin shaped article. Various attempts have been made in the prior art in this regard. For example, a synthetic resin to be shaped is compounded with a sufficient amount of an electroconductive particulate material such as a metal powder or carbon 25 black before molding into a shaped article. Surface resistivity of a synthetic resin shaped article can be decreased when provided with a very thin electroconductive film of a metal formed thereon by the techniques of sputtering, vapor deposition or other suitable method. Static electricity on the surface can be decreased by increasing the hydrophilicity of the surface by the use of a surface active agent as an antistatic agent which may be either incorporated into the 30 body of the article by the admixture of the resin therewith prior to molding, or applied by coating on the surface of the shaped article. Alternatively, introduction of hydrophilic groups or structure to the surface of a shaped article is also effective to decrease the static electricity, as is obtained by a chemical treatment, e.g. acid etching, flame treatment, surface grafting by means of actinic rays such as electron beams, ultraviolet light or ionizing radiation. 30
- 35 These known methods are effective, to some extent, but usually are insufficiently effective in improving antistatic performance, or cause adverse effects on the characteristics of the bulk shaped article, involve extremely high costs, and are applicable only to relatively small articles or treatment in small quantities. 35
- A method according to the present invention, intended to improve the antistatic performance 40 of a synthetic resin shaped article, comprises treating the article by the steps of (a) forming a cross-linked layer in at least the surface stratum of the shaped article; and (b) exposing the surface of the thus-obtained article to low temperature plasma generated in an atmosphere containing a gaseous silicon compound of the formula 40
- 45 $R_aH_bSiX_{4-a-b}$ (I) 45
- in which R, or a combination of any two R's, is an organic radical, X is halogen or alkoxy, a is 0, 1, 2 or 3 and b is 0 or (except when a is 3) 1, or a hydrolysis-condensation product thereof, to such an extent that a plasma-polymerised surface film of the silicon compound having a 50 thickness of at least 5 nm (nanometers) is formed in stratification on the cross-linked layer. 50
- The resin of the shaped article to be treated by the method of the invention may be, for example, thermoplastic or thermosetting. Examples of suitable synthetic resins are polyethylenes, polypropylenes, polystyrenes, saturated and unsaturated polyesters, cellulose acetates, polysulphones, polycarbonates, polyurethanes, polyimides, polyamides, i.e. various types of 55 nylons, polyamidoimides, polyvinyl alcohols, acrylic resins, polyacetals, polyvinyl chlorides, copolymers of styrene and acrylonitrile, copolymers of styrene, acrylonitrile and butadiene, copolymers of ethylene and vinyl acetate, copolymers of vinylidene chloride and vinyl chloride, urea-formaldehyde resins, melamine-formaldehyde resins, phenol-formaldehyde resins, silicone resins, polyphenylene oxides, poly-p-xylenes, epoxy resins and diallyl phthalate resins. 55
- 60 Block copolymers and graft copolymers as well as polymer blends based on these polymers are also suitable. 60
- The shaped article is of course not necessarily formed of one or more of the above named synthetic resins alone but it is optional that the resin is compounded with various kinds of conventional additives and processing aids including, for example, plasticizers, stabilizers, 65 lubricants, fillers, extenders, pigments, dyes, heat-resistance improvers, flame retardants, 65

antioxidants, light absorbers, surface active agents, crosslinking agents, anti-fogging agents, dehumidifiers and elasticity-improvers.

The method of shaping of the articles is also not limitative, including casting, extrusion molding, injection molding, calendering, compression molding and other techniques conventionally used in the fabrication of synthetic resin articles. The form of the shaped article is also not limitative provided uniform exposure of the surface to the low temperature plasma may be obtained. It is also optional that the shaped article is subjected to a desired pretreatment according to need, such as heat treatment, stretching or drawing, crimping, crosslinking, sand-blasting, corona discharge, solvent treatment or irradiation with ionising radiation, whereby the effectiveness of the inventive method is not affected.

The first step of the inventive method is the formation of a crosslinked layer in at least the surface portion of the shaped article, by suitable surface treatment. Various known methods are applicable to this object, including irradiation with actinic rays such as ultraviolet light, electron beams, ionizing radiation, e.g. gamma-rays, treatment with low temperature plasma generated by glow discharge or corona discharge, light irradiation of the shaped article impregnated in advance with a photosensitizer, crosslinking reaction between the polymer molecules and a crosslinking agent contained in the resin composition of the shaped article by incorporating prior to molding or by dipping of the shaped article therein, crosslinking reaction between the molecules of the polymeric resin per se having a crosslinkable structure or being provided with crosslinkable functional groups bonded to the backbone structure thereof, and crosslinking by heating. It is preferable that a surface layer of at least about 2 nm thickness of the shaped article is brought to the crosslinked state by the crosslinking treatment.

The second step of the inventive method is the exposure of the surface thus provided with the crosslinked layer to an atmosphere of low temperature plasma containing the specified silicon compound, or a hydrolysis-condensation product thereof. In the given formula, R may be a monovalent hydrocarbon group exemplified by alkyl such as methyl, ethyl, propyl or butyl, alkenyl such as vinyl or allyl, alkynyl such as ethynyl, propynyl or butynyl, aryl such as phenyl or naphthyl, and such groups substituted by, for example, halogen atoms or cyano groups. X is halogen such as chlorine (preferred), bromine or iodine, or alkoxy such as methoxy, ethoxy or butoxy. At least one atom or group denoted by X is present.

An example of a silicon compound represented by the formula $RHSiX_2$ is methylchlorosilane; examples of those represented by the formula R_2HSiX are dimethylchlorosilane and dimethylmethoxysilane; examples of those represented by the formula R_3SiX are trimethylchlorosilane, trimethylmethoxysilane, trimethylethoxysilane, vinyltrimethylchlorosilane, vinyltrimethylmethoxysilane, vinyltrimethylethoxysilane, ethynyltrimethylmethoxysilane, ethynyltrimethylchlorosilane, triethylmethoxysilane, dimethylchloromethylmethoxysilane, dimethylchloromethylchlorosilane, dimethylphenylmethoxysilane, 2-chloroethyltrimethylchlorosilane and 2-chloroethyltrimethylmethoxysilane; examples of those represented by the formula R_2SiX_2 are methylchloromethylmethoxysilane, dimethylchlorosilane, dimethylmethoxysilane, diethylmethoxysilane, dimethyldichlorosilane, vinylmethyldichlorosilane, 2-chloroethylmethyldichlorosilane, vinylmethyldiethoxysilane, methylchloromethyldichlorosilane, methylphenyldimethoxysilane and methylchloromethyldimethoxysilane; examples of those represented by the formula $RSiX_3$ are methyltrimethoxysilane, methyltriethoxysilane, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, chloromethyltrimethoxysilane, 2-chloroethyltrimethoxysilane and 3-chloropropyltrimethoxysilane; and examples of those represented by the formula SiX_4 are silicon tetrachloride, orthomethyl silicate and orthoethyl silicate. In these examples, X is always chlorine, but the corresponding compounds in which X is bromine or iodine may also be suitable.

In addition to the above named silicon compounds in which the group or groups denoted by R are all unsubstituted or halogen-substituted monovalent hydrocarbon groups, those organosilane compounds having one or more of monovalent hydrocarbon groups or alkoxy groups substituted with a reactive or functional group are also used in the inventive method. Several of the examples of such organosilane compounds, known to be useful as a so-called silane coupling agent in the resin and rubber processing technology, are vinyltris(2-methoxyethoxy)silane, 3-glycidyloxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, [N-(2-aminoethyl)-3-aminopropyl]methyldimethoxysilane, 3-mercaptopropyltrimethoxysilane and 3-aminopropyltriethoxysilane.

As is mentioned before, the silicon compound as an essential constituent of the plasma atmosphere in the inventive method is not limited to the above-named ones which belong to the class of organic or inorganic silane compounds but may be a hydrolysis-condensation product thereof obtained by the partial or complete hydrolysis of the silane compound followed by a partial or complete condensation reaction between the silanolic hydroxy groups formed by the hydrolysis to form one or more siloxane linkages. Exemplary of such a siloxane compound are divinyltetramethyldisiloxane, di(chloromethyl)tetramethyldisiloxane, diethynyltetramethyldisiloxane, 1,1,3,3-tetramethyldisiloxane and other disiloxane compounds. Trisiloxanes and higher

condensates may be used provided that the vapor pressure of the siloxane compound is sufficiently high to sustain the plasma discharge in the atmosphere, which can take place only in an atmosphere of a pressure in a limited range as mentioned below.

The procedure for the low temperature plasma treatment of a shaped article per se is well known in the art. That is, the synthetic resin shaped article, after completion of the step (a) treatment of crosslinking, is brought into a plasma chamber provided with electrodes connected to an electric power source such as a high frequency generator and, after evacuation of the plasma chamber, the chamber is filled with a vapor or gas of the silicon compound to give a pressure of 0.001 to 10 Torr, followed by the supply of electric power to the electrodes to generate low temperature plasma in the plasma chamber, whereby the surface of the shaped article is exposed to the low temperature plasma while the gas of the silicon compound is continuously passed therethrough to control and maintain the pressure.

It is optional according to need that the gas or vapor of the silicon compound is diluted with other kinds of inorganic or organic gases including inert gases, e.g. helium and argon, nitrogen, oxygen, air, hydrogen, carbon monoxide and carbon dioxide, as well as organic gases other than silicon-containing compounds.

As is mentioned above, the pressure inside the plasma chamber should preferably be kept in the range from 0.001 to 10 Torr. This is because the desired low temperature plasma cannot be generated with stability in the plasma chamber and hence no satisfactorily effective plasma treatment can be obtained when the pressure inside the chamber is outside this range. More preferably, the pressure should be in the range from 0.05 to 1 Torr. It has been rather unexpected from the information obtained in the prior art plasma treatment or plasma polymerization that, even when the low temperature plasma treatment has been undertaken prolongedly, the effect of the treatment rapidly decreases and the surface resistivity of the synthetic resin article after plasma treatment increases as the pressure in the plasma atmosphere increases over 10 Torr.

The conditions for the generation of low temperature plasma in the plasma chamber are well known in the art so that no detailed explanation is necessary here. In short, low temperature plasma can be generated in the plasma chamber when electric power of several watts, preferably, at a high frequency range of several kHz to several hundreds of MHz is supplied to the electrodes positioned inside or outside the plasma chamber in which the pressure is kept, as mentioned above. The type of the plasma discharge may be either glow discharge or corona discharge, by which sufficient improvement can be obtained in the surface properties of the thus-treated shaped article. The time for the low temperature plasma treatment may widely differ depending on various factors including the type of the synthetic resin, the power for the plasma generation, and the thickness of the plasma-polymerized film formed on the surface of the shaped article.

It is essential that the plasma-polymerized film of the silicon compound formed on the surface of the shaped article in the above described manner should have a thickness of at least 5 nm. When the thickness is smaller than 5 nm, the antistatic performance of the thus plasma-treated shaped article is unsatisfactory. The upper limit of the thickness is, on the other hand, not critical, provided that the characteristics of the shaped article in bulk are not adversely affected by the prolonged plasma treatment. In this connection, the low temperature plasma treatment of a duration in which the thickness of the plasma-polymerized surface film has a thickness of 1000 nm or smaller can be performed safely without the above-mentioned adverse effects. At any rate, an excessively thick plasma-polymerized surface film should be avoided in order to have good productivity of the process, since the effectiveness of the inventive method does not increase much by increase of the film thickness over an adequate range.

It should be mentioned that, in the low temperature plasma treatment in an atmosphere containing a silicon compound, two kinds or more of the silicon compounds may be used in combination, whereby certain synergistic effects can be achieved in some cases. It may be also advantageous, in order to impart the shaped article with other desirable improved surface properties other than the antistatic performance, to admix the silicon compound with one or more other types of organic compounds and/or the above-mentioned inorganic gases whereby, in addition to the very durable antistatic performance with decreased surface resistivity, the shaped article may be imparted with improved wettability, susceptibility to adhesive bonding, printability, anti-wearing resistance, mold-releasability, heat-resistance, water-resistance, and resistance against migration of ingredients contained therein.

When the plasma-polymerized surface film is formed in accordance with the above described procedure of the inventive method on the surface of the crosslinked layer of the synthetic resin shaped article, the thickness of the plasma-polymerized surface film is usually in the range from 5 to 1000 nm, so that the appearance of the shaped article remains unchanged. Despite the seemingly unchanged appearance of the shaped article, the formation of the crosslinked layer and the plasma-polymerized surface layer can be confirmed by the following methods; for example, the crosslinked layer in the surface portion of the shaped article can be observed by

testing the gelled fraction insoluble in an organic solvent, by examination of the changes in heat resistance and mechanical properties such as tensile and impact strength by measurement of the changes in the molecular weight of the resin by gel permeation chromatography or measurement of the melt viscosity of the resin after treatment, and by examination of decrease in the crystallinity of the resin by the techniques of X-ray diffractometry or infrared spectrophotometry. The formation of the plasma-polymerized surface film, on the other hand, can be confirmed by X-ray photoelectron spectrometry (ESCA) and reflective infrared spectrophotometry indicating that the surface film contains silicon atoms and silicon-to-carbon linkages. Alternatively, the treated shaped article is dyed with osmic acid and then a cross-section of the thus-dyed article is examined by a transmission-type electron microscope: the plasma-polymerized surface film is dyeable with osmic acid whereas the crosslinked layer remains undyed.

The following Experiments illustrate the invention and also comparative procedures.

Experiment 1.

A resin composition composed of 100 parts by weight of a polyvinyl chloride resin, 2 parts by weight of a barium- and zinc-containing stabilizer, 5 parts by weight of triallyl isocyanurate as a crosslinking agent and 0.5 parts by weight of dicumyl peroxide was milled in a hot roller mill at 160°C for 10 minutes and shaped by compression molding with heating at 165°C into a crosslinked polyvinyl chloride resin sheet having a thickness of 0.5 mm, which is referred to as sheet A hereinbelow.

Separately, another polyvinyl resin sheet having a thickness of 0.5 mm was prepared of a resin composition composed of 100 parts by weight of the same polyvinyl chloride resin as above and 2 parts by weight of the barium- and zinc-containing stabilizer alone by compression molding under the same conditions as above and the sheet was subjected to a low temperature plasma treatment for 10 minutes in a plasma chamber which was first evacuated to a vacuum of about 10^{-3} Torr followed by the introduction of vapor of aniline to keep the pressure inside the chamber at 0.3 Torr under continuous flow of the aniline vapor and supply of a high frequency electric power of 200 watts at a frequency of 13.56 MHz to the electrodes of the plasma chamber. The thus plasma-treated resin sheet is referred to as sheet B herein-below.

A portion of each of the above prepared sheets A and B was dipped and dissolved in tetrahydrofuran to determine the gel fraction insoluble in the solvent, from which formation of crosslinked layer was confirmed.

In the next place, the sheets A and B were placed in a plasma chamber and subjected to a low temperature plasma-polymerization treatment for 1 minute by the supply of a high frequency electric power of 1 kilowatt at 13.56 MHz to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-4} Torr followed by the introduction of the atmospheric air to keep the pressure of the inside of the chamber at 0.1 Torr with continuous flow of the air and then continuous introduction of vapor of chloromethyldichlorosilane to be admixed with the flowing air so as to keep the partial pressures of the air and the silane in the chamber at 0.1 Torr and 1.2 Torr, respectively, during the plasma discharge. The resin sheets thus subjected to the plasma-polymerization treatment are referred to as sheets A* and B*, respectively, hereinbelow.

The sheets A* and B* were examined by the methods of X-ray photoelectron spectrometry and reflective infrared spectrophotometry to find that the formation of a plasma-polymerized layer of about 45 nm thickness on each of the sheets was confirmed by the presence of the silicon atoms and the silicon-to-carbon linkages.

The antistatic performance of each of the above sheets A, B, A* and B* was evaluated by the measurements of the distance of cigarette ash attraction, surface resistivity and electrostatic voltage induced by rubbing by the procedures described hereunder. The results of the measurements were as tabulated below.

	Distance of cigarette ash attraction cm	Surface resistivity ohm	Charge voltage by rubbing, volts	
Sheet A*	3	1×10^{12}	1600	
Sheet A	6	7×10^{12}	7600	
Sheet B*	0	3×10^8	200	
Sheet B	6	7×10^{12}	7600	

Distance of cigarette ash attraction: the resin sheet was rubbed 10 times with a dry cotton cloth to be charged with static electricity induced by rubbing and the thus-charged resin sheet

was brought toward a pile of cigarette ash in an atmosphere at 25°C and with 60% relative humidity and the distance between the ash and the sheet at which the ash was first attracted to the sheet was recorded.

Surface resistivity: measurement was performed in an atmosphere of 60% relative humidity by use of an instrument Model SM-10E manufactured by Toa Denpa Kogyo Co. 5

Charge voltage by rubbing: measurement was performed by use of a rotary static tester manufactured by Koa Shokai Co. using a cotton cloth for rubbing the resin sheet under a load of 200 g at 750 r.p.m. for 60 seconds.

10 Experiment 2. 10

A resin sheet of 0.3 mm thickness was prepared from a resin composition composed of 100 parts by weight of a vinyl chloride resin and 50 parts by weight of dioctyl phthalate. This resin sheet was irradiated with ultraviolet light for 2 minutes in an atmosphere of reduced pressure of air at 10 Torr under a low-pressure mercury lamp of 300 watts output emitting line spectra at 15 185 nm, 254 nm, 313 nm and 365 nm held 5 cm apart above the sheet. The thus ultraviolet-irradiated resin sheet is referred to as sheet C hereinbelow. 15

Sheet C was placed in a plasma chamber and subjected to a low temperature plasma-polymerization treatment for 30 seconds by the supply of a high frequency electric power of 2 kilowatts at 13.56 MHz to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-3} Torr followed by the introduction of the atmospheric air to keep the pressure of 20 the inside of the chamber at 0.05 Torr with continuous flow of the air and then continuous introduction of vapor of orthomethyl silicate to be admixed with the air so as to keep the partial pressures of the air and the silicon compound in the chamber at 0.05 Torr and 0.6 Torr, respectively, during the plasma discharge. The resin sheet thus subjected to the plasma- 25 polymerization treatment is referred to as sheet C* hereinbelow. 25

This sheet C* was dyed with osmic acid and a section thereof was examined with a transmission-type electron microscope to find the presence of an undyed crosslinked layer of about 100 nm thickness in the surface portion of the sheet overlaid with a dyed layer of about 85 nm thickness which was a plasma-polymerized surface film of the silicon compound. 30 Each of the sheets C and C* was subjected to the test for the antistatic performance in the same manner as in Experiment 1 above to give the results shown below. 30

	Distance of cigarette ash attrac- tion, cm	Surface resistivity, ohm	Charge volt- age by rub- bing, volts	
35 Sheet C*	0	6×10^8	350	35
40 Sheet C	5	4×10^{13}	4200	40

Experiment 3.

A low-density polyethylene film of 0.3 mm thickness obtained on the market, which is referred to as film D hereinbelow, was irradiated with electron beams of 2 MeV energy in an 45 evacuated atmosphere to effect crosslinking between the polyethylene molecules at the surface portion. The thus surface-crosslinked resin film is referred to as film E hereinbelow. 45

On the other hand, another portion of the same polyethylene film was placed in a plasma chamber and subjected to the exposure to low temperature plasma produced in the chamber to effect crosslinking at the surface portion by the supply of a high frequency electric power of 100 50 watts at 13.56 MHz for 3 minutes to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-4} Torr followed by the continuous introduction of helium so as to keep the pressure inside of the chamber at 0.5 Torr during the plasma discharge. The thus plasma-treated polyethylene film is referred to as film F hereinbelow. Each of the films E and F 55 was dissolved in hot xylene, causing precipitation of an insoluble gelled fraction, indicating the crosslinking of the resin molecules. 55

Films E and F were placed in a plasma chamber and subjected to a low temperature plasma-polymerization treatment by the supply of a high frequency electric power of 10 kilowatts at 110 kHz for 20 seconds to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-3} Torr followed by the continuous introduction of vapor of divinyltetramethyldi- 60 siloxane so as to keep the pressure inside the chamber controlled at 0.5 Torr during the plasma discharge. The resin films thus subjected to the plasma-polymerization treatment are referred to as films E* and F*, respectively. The thickness of the plasma-polymerized surface films on the films E* and F* was about 15 nm as examined in the same manner as in Experiment 2. 60

Each of the films D, E, F, E* and F* was subjected to the test for the antistatic performance in 65

the same manner as in Experiment 1 to give the results shown below.

	Distance of cigarette ash attrac- tion, cm	Surface resistivity, ohm	Charge volt- age by rub- bing, volts	
5				5
Film E*	1	7×10^9	700	
10 Film E	7	8×10^{15}	9500	10
Film F*	1	1×10^{10}	600	
Film F	6	4×10^{15}	7700	
Film D	6	6×10^{15}	8600	

15 *Experiment 4.* 15

A resin film of 0.5 mm thickness, of a 85:15 by weight copolymer of vinylidene chloride and vinyl chloride obtained on the market, which is referred to as film G hereinbelow, was placed in a plasma chamber and subjected to exposure to low temperature plasma for 5 minutes to effect crosslinking of the surface portion by the supply of a high frequency electric power of 500 watts at 110 kHz to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-3} Torr followed by the continuous introduction of nitrogen and argon so as to keep the partial pressures of nitrogen and argon at 0.2 Torr and 0.1 Torr, respectively, in the chamber during the plasma discharge. The thus plasma-crosslinked resin film is referred to as film H hereinbelow. 20 25

The film H was dyed with osmic acid and a section thereof was examined by use of a transmission-type electron microscope to find the presence of an undyed surface layer of about 200 nm thickness in the surface portion of the dyed resin film, indicating crosslink formation in the surface portion. 30

The film H in the plasma chamber was then subjected to the plasma-polymerization treatment for 5 minutes by the supply of a high frequency electric power of 200 watts at 13.56 MHz to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-3} Torr followed by the continuous introduction of vapor of vinyltrimethylmethoxysilane so as to keep the pressure inside the chamber at 0.05 Torr during the plasma discharge. The resin film thus subjected to the plasma-polymerization treatment is referred to as film H* hereinbelow. This film H* was examined with a transmission-type electron microscope after dyeing with osmic acid in the same manner as above to find the presence of a dyed surface film of about 200 nm thickness formed on the above mentioned undyed crosslinked layer. 35

Each of the films G, H and H* was subjected to the test for the antistatic performance in the same manner as in Experiment 1 to give the results shown below. 40

	Distance of cigarette ash attrac- tion, cm	Surface resistivity, ohm	Charge volt- age by rub- bing, volts	
45				45
Film H*	0	6×10^8	250	
Film H	8	9×10^{14}	9600	
50 Film G	8	9×10^{14}	9200	50

Experiment 5.

A commercially-available stretched resin film of polyethylene terephthalate having a thickness of about 0.3 mm, which is referred to as film I hereinbelow, was irradiated with gamma-rays from Co-60 in a radiation dose of about 10 Mrad to effect crosslinking of the resin. This irradiated resin film was dissolved in a solvent mixture of phenol and tetrachloroethylene, causing precipitation of a considerable amount of insoluble gelled fraction, indicating the formation of crosslinks. The thus-crosslinked polyethylene terephthalate film is referred to as film J hereinbelow. 55 60

This film J was placed in a plasma chamber and subjected to the treatment of plasma-polymerization for 2 minutes by the supply of a high frequency electric power of 500 watts at 13.56 MHz to the electrodes of the plasma chamber, which was first evacuated to a vacuum of 10^{-3} Torr followed by the continuous introduction of vapor of trimethylmethoxysilane so as to keep the pressure of inside of the chamber at 0.6 Torr during the plasma discharge. The resin 65

film thus subjected to the treatment of plasma polymerization is referred to as film J* hereinbelow.

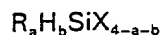
The formation of a plasma-polymerized surface film on this film J* was confirmed by the X-ray photoelectron spectrometry and the reflective infrared spectrophotometry showing the presence of silicon atoms and silicon-to-carbon linkages in the surface film which had a thickness of about 20 nm.

Each of the films I, J and J* was subjected to the test for the antistatic performance in the same manner as in Experiment 1 to give the results shown below.

	Distance of cigarette ash attraction, cm	Surface resistivity, ohm	Charge voltage by rubbing, volts
Film J*	1	7×10^9	450
Film J	5	2×10^{13}	6000
Film I	6	1×10^{14}	6500

CLAIMS

1. A method for treating a shaped article of a synthetic resin, which comprises the steps of (a) forming a cross-linked layer in at least the surface stratum of the shaped article; and (b) exposing the surface of the thus-obtained shaped article to low temperature plasma generated in an atmosphere containing a gaseous silicon compound of the formula



in which R, or a combination of any two R's, is an organic radical, X is halogen or alkoxy, a is 0, 1, 2 or 3 and b is 0 or (except when a is 3) 1, or a hydrolysis-condensation product thereof, to form a plasma-polymerised surface film, at least 5nm thick, of the silicon compound.

2. A method as claimed in claim 1, wherein the crosslinked layer is at least 2 nm thick.

3. A method as claimed in claim 1 or claim 2, wherein R is alkyl, alkenyl, alkynyl or aryl.

4. A method as claimed in any preceding claim, wherein X is chlorine.

5. A method as claimed in any of claims 1 to 3, wherein X is methoxy, ethoxy or butoxy.

6. A method as claimed in any preceding claim, wherein the silicon compound is in the form of a hydrolysis-condensation product selected from divinyltetramethyldisiloxane, di(chloromethyl)tetramethyldisiloxane, diethynyltetramethyldisiloxane and 1,1,3,3-tetramethyldisiloxane.

7. A method as claimed in claim 1, substantially as herein described with reference to the production of films B*, C*, E*, F*, H* and J*.